

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets

SCIENCE REFERENCE LIBRARY

(11) Publication number:

0 130 632
A2

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 84200767.6

(22) Date of filing: 25.05.84

(51) Int. Cl.: C 08 F 2/32

(30) Priority: 26.05.83 US 498222

(43) Date of publication of application: 09.01.85
Bulletin 85/2

(84) Designated Contracting States: DE FR NL

(71) Applicant: THE DOW CHEMICAL COMPANY, Dow
Center 2030 Abbott Road Post Office Box 1967, Midland
Michigan 48640 (US)

(72) Inventor: Emerson, Richard R., 628 Hillcrest, Midland
Michigan 48640 (US)
Inventor: Lee, Do Ik, 5109 Nakoma Drive, Midland
Michigan 48640 (US)
Inventor: Easterly, James P., 5038 Reinhardt, Bay City
Michigan 48706 (US)

(74) Representative: Urbanus, Henricus Maria, Ir. et al, c/o
Vereenigde Octrooibureaux Nieuwe Parklaan 107,
NL-2587 BP 's-Gravenhage (NL)

(54) Water-in-oil emulsion polymerization processes and the water-in-oil emulsions prepared therefrom.

(57) This invention is directed to a water-in-oil emulsion polymerization process for preparing polymers of water-soluble monomers and to the water-in-oil emulsions prepared by the process. The process comprises subjecting portions of the emulsion to varying rates of shear during emulsion formation. Emulsions comprising water-soluble polymers prepared by this process contain a discontinuous aqueous phase having two or more droplet size distributions. These emulsions can have high polymer solids, reduced oil content, low bulk viscosity and high stability.

EP 0 130 632 A2

BEST AVAILABLE COPY

THIS PAGE BLANK (USPTO)

0130632

WATER-IN-OIL EMULSION POLYMERIZATION PROCESSES
AND THE WATER-IN-OIL EMULSIONS PREPARED THEREFROM

This invention relates to water-in-oil emulsion polymerization processes and to the water-in-oil emulsions prepared therefrom.

Various water-soluble polymers such as poly-
5 acrylamide and copolymers of acrylamide with other
anionic, cationic or nonionic monomers are well-known
to be precipitants or flocculants for many substrates
including sewage, cellulosic fibers and fines for
retention and freeness, effluent waste for metal produc-
10 tion, coal tailings and the like. Such polymers are
also known to exhibit superior thickening properties
when said polymers are dissolved in aqueous media.
Particularly well-known for this purpose are the anionic
polyacrylamides such as acrylamide/acrylic acid copoly-
15 mers, including those prepared by hydrolysis of poly-
acrylamide. Such polymers are also very useful as
fluid mobility control agents in enhanced oil recovery
processes.

In the past, such polymers have been made
20 available commercially as powders or finely divided
solids which must be subsequently dissolved in an

0130632

aqueous medium in order to be used. Because such dissolution steps are sometimes time consuming and often require rather expensive mixing equipment, it has become a common practice to formulate the water-soluble polymers in water-in-oil emulsions wherein the polymer is dissolved in the dispersed aqueous phase. Such emulsions, as well as methods for preparing them, are described in U.S. Patent No. 3,284,393 to Vanderhoff et al. In order to accelerate the inversion (i.e., solubilization) rate of such emulsions, it has been a common practice, for example, as shown in U.S. Patent No. RE 28,474, to add a water-soluble surfactant to the emulsion during or just prior to inversion. While the foregoing procedures generally do overcome the problems of dissolving dry powders of water-soluble polymers in aqueous media, such emulsions contain substantial quantities of water and oil, thus increasing the cost of manufacturing, shipping and handling such polymers to a significant degree. In addition, the stability of such emulsions after storage for significant periods is often very poor.

In an attempt to employ less quantities of water and oil in said emulsion, it is taught in U.S. Patent No. 4,052,353 to concentrate such emulsions by removing water from the emulsions and subsequently adding sufficient water-soluble surfactant to render the water-soluble polymer self-dissolving in water. Unfortunately, however, the stability of such emulsions after storage for significant periods is not as high as is desirable. Other attempts to employ less quantities of oil in said emulsions have been made by decreasing the oil phase of said emulsions while holding the polymer-water phase constant, as taught in U.S.

0130632

Patent No. 3,826,771. Unfortunately, the bulk viscosity of said emulsions increases severely, and limits such attempts to concentrate conventional emulsions.

U.S. Patent No. 3,996,180 teaches a process
5 for preparing water-in-oil emulsions of water-soluble polymers. The process comprises subjecting the water-in-oil emulsion of the water-soluble monomer to high shear mixing prior to polymerization. ~~It is noted in~~
10 this patent that the emulsion may become thick due to the decreased average particle size of the monomer phase contained within the emulsion.

In view of the foregoing deficiencies of conventional emulsions and concentrated dispersions derived from such emulsions, it is highly desirable to
15 provide a water-in-oil emulsion of a water-soluble polymer that can be inverted quickly into an aqueous medium, can be stored for substantial periods of time without losing stability, contains a high polymer content, and yet exhibits a low bulk viscosity.

20 The present invention is a water-in-oil emulsion polymerization process for preparing polymers of water-soluble monomers which comprises:

- (1) preparing a stable water-in-oil emulsion by:
 - 25 (a) providing an aqueous solution comprising water and at least one water-soluble monomer,
 - (b) providing an oil solution comprising an inert hydrophobic organic liquid,
 - 30 (c) mixing a portion of the aqueous solution to the oil solution in an amount sufficient to form an aqueous dispersed phase,

0130632

- (d) subjecting the mixture to a shear rate at least sufficient to form a portion of said water-in-oil emulsion,
- (e) admixing an additional portion of the aqueous solution to the resulting portion of the emulsion previously prepared in an amount sufficient to form an aqueous dispersed phase, and
- (f) subjecting the resulting mixture to a shear rate progressively lower than that employed in forming the previous portion of the emulsion,
- (g) wherein steps (e) and (f) are performed at least once until said water-in-oil emulsion is formed, and
- (2) subjecting the resulting emulsion to polymerization conditions.

The process described above may be modified as follows. Step (1)(c) comprises mixing a portion of the aqueous solution with a portion of the oil solution in an amount sufficient to form an aqueous dispersed phase, step (1)(e) comprises admixing an additional portion of the aqueous solution to an additional portion of the oil solution in an amount sufficient to form an aqueous dispersed phase, step (1)(f) comprises forming a water-in-oil emulsion by subjecting the resulting mixture to a shear rate progressively lower than that employed in forming the previous portion of the emulsion, and new step (1)(h) comprises mixing portions from steps (1)(d) and (1)(f) together to yield said water-in-oil emulsion. The process just described may be even further modified as follows: step (1)(h) is omitted, step (2) comprises subjecting each of the water-in-oil

emulsions from steps (1)(d) and (1)(f) to polymerization conditions, and new step (3) comprises mixing together the various water-in-oil emulsions of water-soluble polymers.

5 The present invention is a water-in-oil emulsion of water-soluble polymer prepared by each of the aforementioned processes.

10 Emulsions can be prepared by incorporating at least one emulsifying surfactant into the process of this invention. Emulsions can also be prepared by incorporating at least one emulsifying surfactant and at least one inverting surfactant into the process of this invention.

15 The emulsions of this invention are superior to conventional emulsions in that they can have higher polymer solids than said conventional emulsions. In addition, the emulsions of this invention can have reduced oil content, lower bulk viscosity and greater stability than are characteristic in the conventionally prepared emulsions which contain comparable amounts of solids. The emulsions of this invention, although
20 generally self-inverting upon the addition to water, are stable enough in that they can be stored for long periods of time and/or can undergo several freeze/thaw cycles without irreversible coagulation or precipitation.
25 These emulsions have the ability to invert readily into aqueous media containing an inverting surfactant and substantial quantities, e.g., from 0.0001 to 20 weight percent, of dissolved salts.

0130632

In addition to their utility as additives in drilling muds, fracturing fluids and fluid mobility control agents in enhanced oil recovery methods, the polymers prepared in accordance with the practice of the present invention are also useful as flocculating agents for sewages, industrial wastes, mining streams such as coal slurries and mining effluents, as thickeners for coating formulations, as additives for the manufacture of paper, and in a variety of other uses common for such polymers prepared by other conventional polymerization methods.

The present invention is practiced in the preparation of water-in-oil emulsions containing any water-soluble polymer. Such emulsions are those wherein the dispersed phase is an aqueous phase having dissolved therein said water-soluble polymer, and the continuous oil phase is a water-immiscible inert organic liquid. In emulsions of this invention, the ratio of the aqueous phase to the oil phase is such that the emulsion contains from 50 to 95, preferably from 70 to 95, weight percent of aqueous phase. Advantageously, the emulsion comprises preferably from 72 to 90, most preferably from 74 to 85, weight percent aqueous phase based on the total weight of the emulsion. The amount of polymer contained in the emulsion can vary providing that the resulting emulsion is stable, and is advantageously from 21 to 80, more preferably from 24 to 75, most preferably from 27 to 70, weight percent polymer based on the total weight of the emulsion. In the emulsions, the weight ratio of water to polymer in the aqueous phase can vary and is desirably from 0.001:1 to 3.4:1, more preferably from 0.01:1 to 2.9:1, and most preferably from 0.08:1 to 2.6:1. The weight ratio of oil to polymer can vary

and is preferably from 0.2:1 to 1:1, more preferably from 0.25:1 to 0.98:1, most preferably from 0.3:1 to 0.95:1.

For the purposes of this invention, the water-soluble polymer contained in the aqueous phase of the emulsion is one that forms a thermodynamically stable mixture when combined with water. These mixtures form spontaneously and include true solutions in which the individual polymer molecules are dispersed as well as micellular or colloidal solutions wherein the polymer molecules are aggregated to some extent, but wherein such aggregates are no larger than colloidal size. Accordingly, such water-soluble polymers are generally homopolymers and copolymers of water-soluble ethylenically unsaturated monomers.

Suitable water-soluble monomers include those that are at least water-miscible and that are preferably sufficiently water-soluble to form at least a 5 weight percent solution when dissolved in water and readily undergo addition polymerization to form polymers that are water-soluble. Exemplary water-soluble monomers include ethylenically unsaturated amides such as acrylamide, methacrylamide and fumaramide; their N-substituted derivatives such as 2-acrylamide-2-methylpropane sulfonic acid (AMPS), N-(dimethylaminomethyl)acrylamide as well as N-(trimethylammoniummethyl)acrylamide chloride and N-(trimethylammoniumpropyl)methacrylamide chloride; ethylenically unsaturated carboxylic acids such as acrylic acid, methacrylic acid, itaconic acid and fumaric acid; ethylenically unsaturated quaternary ammonium compounds such as vinylbenzyl trimethyl ammonium chloride, sulfoalkyl esters of unsaturated car-

0130632

boxylic acids such as 2-sulfoethyl methacrylate; amino-alkyl esters of unsaturated carboxylic acids such as 2-aminoethyl methacrylate and 2-(N,N-dimethylamino)-ethyl methacrylate as well as the quaternized derivatives thereof such as acryloylethyl trimethyl ammonium chloride; vinyl amines such as vinyl pyridine and vinyl morpholine, diallyl amines and diallyl ammonium compounds such as diallyl dimethyl ammonium chloride; vinyl heterocyclic amides such as vinyl pyrrolidone; vinylaryl sulfonates such as vinylbenzyl sulfonate as well as the salts of the foregoing monomers. Of the foregoing water-soluble monomers, acrylamide and combinations of acrylamide and acrylic acid are preferred. Homopolymers of acrylic acid can also be prepared.

Homopolymers prepared from acrylamide and copolymers prepared from combinations thereof with other water-soluble monomers are more preferred. Also preferred are polymers wherein the water-soluble monomers range from 60 to 99 mole percent of acrylamide and/or partially hydrolyzed acrylamide from 1 to 40 mole percent of other water-soluble monomers.

The molecular weight of the water-soluble polymer is not particularly critical and may vary over a wide range from 100,000 to 25 million depending on the desired use of the polymer. Preferred polymers have weight average molecular weight in the range from 2 to 10 million.

The water-immiscible oil phase of the emulsion generally comprises at least one inert hydrophobic liquid. Usually such liquid is an organic liquid such as a liquid hydrocarbon or substituted hydrocarbon. Preferred organic liquids are the halogenated hydro-

0130632

carbons such as, for example, perchloroethylene or methylene chloride as well as liquid hydrocarbon having from 4 to 15 carbons per molecule including aromatic and aliphatic hydrocarbons and mixtures thereof, such as, for example, benzene, xylene, toluene, mineral oils or liquid paraffins such as kerosene or naphtha. Of the foregoing organic liquids, the hydrocarbons are the more preferred, with aliphatic hydrocarbons being most preferred.

10 The water-in-oil emulsions are prepared by following the general procedure described in the prior art as exemplified in U.S. Patent Nos. 3,284,393; RE 28,474; RE 28,576 and 4,376,850. In such methods, an aqueous solution of water-soluble, ethylenically
15 unsaturated monomer(s) is dispersed in the inert hydrophobic organic liquid containing a sufficient amount of a water-in-oil emulsifying surfactant to form a water-in-oil emulsion of the water-soluble monomer(s).

 Broadly speaking, the emulsions of this
20 invention are referred to as multi-modal water-in-oil emulsions. Specifically, water-in-oil emulsions of this invention are prepared by obtaining varying sets of dispersed aqueous phase droplets of differing diameters (i.e., size distributions) by employing
25 separate emulsification steps. One embodiment of the process for preparing such emulsions can involve the preparation of a set of small droplets by adding a desired portion of the aforementioned aqueous solution to the oil solution, which preferably contains at least
30 one emulsifying surfactant, and subjecting the mixture to high shear. To this water-in-oil emulsion is added another desired portion of aqueous solution. This

0130632

mixture is then subjected to a lower shear rate than previously employed to yield an emulsion having two distinguishable droplet size distributions each of which exhibit a dispersion or cluster of droplet sizes about two mean values. Alternatively, a portion of the aqueous solution can be mixed with a portion of the oil solution, which preferably contains one or more surfactants, and subjected to high shear, while the remaining portion of the aqueous solution and the remaining oil solution are mixed and subjected to another rate of shear. The two (or more) emulsions so formed can then be mixed and agitated. The aforementioned processes can be repeated indefinitely using varying proportions of aqueous solution and varying shear rates until all of the aqueous solution is exhausted. It is necessary that the process be carried out to, at least, yield a bimodal system.

Another embodiment of the process for preparing the multi-modal emulsions of this invention includes mixing portions of the aqueous solution with the oil solution, which preferably contains at least one emulsifying surfactant, and subjecting the mixture to high shear as described hereinbefore to yield an emulsion comprising small size droplets. This process of adding the aqueous solution to the oil solution or to the water-in-oil phase can be repeated several times using progressively lower shear rates, if desired, and the remaining portion of the aqueous solution is added to the reactor together with said emulsion, wherein the resulting mixture is agitated using the reactor agitator to yield a portion of large size droplets. For example, in one embodiment of this invention, a bimodal emulsion is prepared by adding a portion of the aqueous solution

to the oil and surfactant solution and subjecting the mixture to high shear. The emulsion so prepared is then added to a reactor together with the remaining portion of the aqueous solution, and the resulting
5 mixture is agitated using the reactor agitator or a static mixer at the lower shear rate to yield a bimodal emulsion.

Another embodiment of the process for preparing the multi-modal emulsions of this invention involves
10 mixing a portion of the aqueous solution which contains the water-soluble monomer with a portion of the oil solution, which preferably contains at least one emulsifying surfactant, and subjecting the mixture to high shear. The remaining portion of the aqueous
15 solution and the remaining portion of the oil solution is mixed and subjected to another rate of shear. The two (or more) emulsions so formed can each be subjected to polymerization conditions as described hereinafter. The two (or more) polymer-containing emulsions so
20 formed are then mixed together.

Varying shear rates are provided by devices such as static mixers, stirrers, inline dispersers, inline mixers, vessel agitators, blenders, ultrasonic homogenizers, or comparable agitating devices. As used
25 herein, the term "shear" is to be broadly construed to include shearing and agitation provided by a wide variety of mixing and/or emulsifying devices. The size of various sets of droplets so prepared is inversely proportional to the rate of shear employed (i.e., the
30 higher the shear rate, the smaller the droplet size). It is also understood that droplet sizes are also affected by factors such as the type of blade employed in the device providing the high shear rate.

The amount of time each emulsion is subjected to a particular shear rate or agitation is generally a significant factor in the width of the droplet size distribution. For example, an emulsion which is
5 subjected to a high shear for a long period of time will generally have a narrow droplet size distribution (i.e., a relatively narrow dispersion of sizes clustered about a mean droplet diameter value). Thus, it is possible to prepare multi-modal emulsions which exhibit
10 separate and distinct droplet size distributions. Conversely, it is possible to prepare multi-modal emulsions which exhibit significant overlap of droplet size distribution by employing shear rates in the preparation of each portion of the water-in-oil emulsion
15 which are not significantly different and/or by subjecting each portion of the emulsion to a short shear time.

It is understood that by employing varying devices which provide varying shear rates and varying
20 mixing, shearing or agitation times which yield various modes of droplets, a very broad droplet size distribution can be obtained. That is, it is possible, for example, to slowly add the aqueous phase to the oil phase while slowly lowering the rate of shear to which
25 the emulsion is subjected. The broad distribution so obtained can represent an average of the various droplet size distributions and resemble one very broad particle size distribution. It is understood that an emulsion having a broad droplet size distribution but prepared
30 via the process of this invention is considered to fall within the scope of this invention.

0130632

The size (i.e., diameter) of the individual sets of droplets of the emulsion can vary. The size of the smallest aqueous phase droplets will vary depending upon the type of high shear device which is employed, the surfactant system employed, and to a much lesser extent, to the length of time that the particular portion of the emulsion is subjected to said shear. The size of the small droplets can be as small as possible as to be within practical limits. That is, the highest shear rates will provide the smallest size droplets.

As previously mentioned, the surfactant system which is employed can affect the size of the aqueous phase droplets. For example, varying amounts and types of surfactants can be added at various times during emulsion preparation. However, surfactant systems affect the size of the aqueous phase droplets and, hence, affect the distribution of droplets of the multi-modal emulsion, to a much lesser extent than do the varying shear rates.

The bimodal emulsion is an example of one of the multi-modal emulsions of this invention. Such a bimodal emulsion comprises small dispersed phase droplets which most desirably cluster about a droplet size which can range from 0.01 μm to 1 μm , preferably from 0.1 μm to 1 μm in diameter. The large dispersed phase droplets can cluster about a droplet size which can range from greater than 1 μm to 40 μm , preferably from 1 μm to 20 μm in diameter. By the term "cluster about a droplet size" is meant that the droplet size distribution is narrow in an identifiable droplet size range. Thus, there preferably exist two identifiable and

0130632

distinct droplet size distributions. Preferably, the diameter of the large droplets is 3 to 100 times that of the diameter of the small droplets. It is most preferable that the ratio of the diameter of the large droplets to that of the small droplets be as large as possible within practical limits. For the bimodal emulsion, the small droplets can contain from 2 to 98, preferably from 20 to 80, most preferably from 30 to 75, weight percent of the total dispersed phase, while the large droplets can contain from 2 to 98, preferably from 20 to 80, most preferably from 25 to 70, weight percent of the total dispersed phase.

Emulsifying surfactants suitably employed for purposes of emulsifying the aqueous phase containing the water-soluble monomer in the organic liquid are those surfactants that promote the formation and stabilization of water-in-oil emulsions. Normally, such surfactants have a hydrophilic-lipophilic balance (HLB) in the range from 2 to 9, most preferably from 3 to 6. Other suitable emulsifying surfactants include, for example, hexadecyl sodium phthalate, decyl sodium phthalate, octadecyl sodium phthalate, sorbitan monooleate, sorbitan stearate, glycerine mono- or distearate and combinations of such emulsifying surfactants. Generally, the emulsifying surfactant is used in amounts sufficient to provide the desired water-in-oil emulsion. This amount is normally in the range from 0.1 to 20, preferably from 3 to 9, weight percent based on the weight of monomer.

Polymerization of the water-in-oil emulsion of the water-soluble monomer(s) is advantageously effected under conventional conditions such as described

0130632

in U.S. Patent Nos. 3,284,393; RE 28,474; RE 28,576 and
4,376,850. Normally, such polymerization is practiced
in the presence of a polymerization initiator capable
of generating free-radicals. Preferably, this free-
5 radical initiator is employed in amounts from 0.01 to
0.1 weight percent of initiator based on the monomers.
Exemplary polymerization initiators include the inorganic
persulfates such as potassium persulfate, ammonium
persulfate and sodium persulfate; azo catalysts such as
10 azobisisobutyronitrile and dimethylazoisobutyrate;
organic peroxygen compounds such as benzyl peroxide,
t-butylperoxide, diisopropylbenzene hydroperoxide,
t-butyl hydroperoxide; and compounds such as sodium
borohydride. Of these initiators, the organic types
15 such as t-butyl hydroperoxide are preferred. In addi-
tion to the aforementioned ingredients, the emulsion
polymerization recipe optionally includes, for example,
chain transfer agents, chelating agents, buffers,
and/or salts.

20 An inverting surfactant is advantageously
incorporated into the emulsion in an amount that is
sufficient to improve the emulsion properties and
stability and to a lesser extent, to lower the bulk
viscosity of emulsion to a value that is at least 5
25 percent lower than the bulk viscosity of the emulsion
prior to addition of the surfactant, provided that said
amount is less than that which destabilizes the emulsion.
By "destabilizing the emulsion" is meant that the
water-in-oil emulsion of water-soluble polymer separates
30 into two phases having a single interface or inverts
into an oil-in-water emulsion. The amount of inverting
surfactant that is employed generally depends upon the
nature of the surfactant. Preferably, said amount of

inverting surfactant that is added is in the range from 0.1 to 200 weight percent based on the weight of the water-in-oil emulsifying surfactant used, more preferably from 1 to 150 weight percent. It is desirable to
5 add some of the inverting surfactant prior to polymerization.

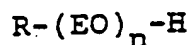
In one preferred embodiment of this invention, an initial portion of inverting surfactant is added to the monomeric precursor, or it is added to the aqueous
10 phase or oil phase prior to formation of the monomeric precursor, so long as it is present in the monomeric precursor prior to the completion of polymerization. Such initial portion of inverting surfactant is usually an amount in the range from 0.1 to 100 weight percent
15 based on the weight of water-in-oil emulsifier used; most preferably from 20 to 40 weight percent. The resulting stable multi-modal water-in-oil emulsion of monomer is then subjected to free-radical forming conditions in order to polymerize the monomer in the
20 dispersed phase to form a water-in-oil emulsion of the water-soluble polymer. Subsequent to polymerization, this emulsion which already contains an initial portion of inverting surfactant is combined with additional inverting surfactant which may or may not be the same
25 as the inverting surfactant added prior to polymerization. This postadded inverting surfactant is added in an amount sufficient to enhance the invertibility of the emulsion, but not enough to destabilize the emulsion. Preferably, this amount of inverting surfactant added
30 after polymerization is in the range from 0.1 to 200, most preferably from 10 to 150, weight percent based on the weight of water-in-oil emulsifier used.

0130632

Also, in yet another embodiment, no inverting surfactant is added prior to polymerization but rather it is added afterwards. Preferably, such an amount of inverting surfactant is in the range from 0.1 to 200, more preferably from 10 to 150, weight percent based on the weight of the water-in-oil emulsifier employed to prepare the emulsion. In the least preferred, but suitable embodiment of this invention, all of the inverting surfactant is added before polymerization.

Inverting surfactants suitably employed in the practice of this invention are generally those that promote the formation of oil-in-water emulsions or dispersions when said emulsion is combined with sufficient water to form a continuous aqueous phase. Generally, such inverting surfactants are water-soluble compounds having an HLB in the range from 6.5 to 20, preferably from 10 to 18. Examples of such inverting surfactants include nonionic, anionic, cationic or amphoteric surfactants with nonionic surfactants being preferred.

Preferred nonionic surfactants include (1) alkyl polyethyleneoxy compounds such as alkyl polyethyleneoxy alcohol represented by the formula:



wherein R is C_4-C_{20} alkyl, EO is ethyleneoxy and n is a number from 1 to 20 and (2) nonionic surfactants such as the reaction products of ethylene oxide or mixtures of ethylene oxide and higher alkylene oxide with active hydrogen compounds such as phenols, alcohols, carboxylic acids and amines, e.g., alkylphenoxyethyleneoxy alcohols and alkylphenoxy polyethyleneoxy alcohols.

Also suitable are anionic compounds represented by the formula:



wherein R is as defined hereinbefore and X is SO_3H , CO_2H or PO_3H and salts thereof. Examples include long chain carboxylates such as potassium oleate, sodium laurate, potassium stearate, potassium caprolate, or sodium palmitate; alkali metal alkylbenzene sulfonates such as sodium nonylbenzene sulfonate and potassium dodecylbenzene sulfonate; alkali metal alkyl sulfates such as sodium dodecyl sulfate and alkali metal dialkyl sulfosuccinates such as sodium dihexyl sulfosuccinate and sodium dioctyl sulfosuccinate; salts of resin acids such as abietic acid and dihydroabietic acid.

Also suitable are cationic surfactants such as alkyl ammonium or quaternary ammonium salts, for example, dodecyl ammonium hydrochloride or dodecyl trimethyl quaternary ammonium chloride, and ethoxylated fatty amines. Other suitable surfactants are described in McCutcheon's Detergents and Emulsifiers, North American Edition, 1980 Annual. Also included in the aforementioned surfactants are oligomeric and polymerizable surfactants described at pages 319-322 of Blackley, Emulsion Polymerization, Halsted Press (1975). Examples of such oligomers include ammonium and alkali metal salts of functionalized oligomers sold by Uniroyal Chemical under the trade name "Polywet" and copolymers of acrylonitrile and acrylic acid having molecular weights less than 2000 which are prepared in the presence of chain terminating agents such as n-octyl mercaptan. Examples of polymerizable surfactants include sodium

0130632

salts of 9- and 10-(acryloylamido)stearic acid. Of the foregoing surfactants, the nonionic types are preferred, with ethoxylated alkyl phenols and ethoxylated fatty alcohols being most preferred.

5 It is possible to concentrate the emulsions prepared via the process of this invention. In concentrating the emulsion, said emulsion is subjected to conditions such that a significant part of water and other volatiles are removed from the emulsion. Such
10 volatilizing conditions can involve heating and/or subjecting the emulsion to reduced pressure in order to volatilize the components to be removed. Preferably, concentration is achieved by subjecting the emulsion to
15 temperatures from 25° to 120°C, most preferably from 40° to 100°C and pressures from 1 to 760 millimeters (mm) of mercury (0.1 to 101 kPa), preferably from 1 to 100 mm of mercury (0.1 to 13.3 kPa). It is understood that the volatiles to be removed may be entirely water or a mixture of water and oil. It is further understood
20 that it is not generally necessary to maintain any particular water to oil ratio in the emulsion during or subsequent to removal of the volatiles.

 The concentrated emulsion is generally self-inverting in that it inverts readily when dispersed
25 into water without the necessary addition of additional inverting surfactant thereto. Such an emulsion is particularly effective for inversion into aqueous media containing from 0.0001 to 20, especially from 0.001 to 5, weight percent of dissolved salts such as, for
30 example, sodium chloride, calcium chloride, or magnesium chloride. When inverting the concentrated emulsions of this invention into more concentrated brines, it is

0130632

often desirable to add additional inverting surfactant to the concentrated emulsion or to the brine prior to inversion.

5 An advantage of the multi-modal emulsions of this invention includes the ability to prepare stable emulsions having higher aqueous phase concentrations than those prepared using conventional emulsification techniques and which are prepared using similar surfactant concentrations. Thus, it is possible through the
10 process of this invention to prepare stable emulsions (i.e., emulsions which do not gel or otherwise fail) with higher solids content than those prepared using conventional emulsion techniques. Another advantage of the multi-modal emulsions is that the bulk viscosity of
15 said multi-modal emulsions is low, as compared to a conventionally prepared emulsion. Yet another advantage of the multi-modal emulsions of this invention concerns the lack of compaction tendencies of said emulsion (i.e., the amount of polymer that coagulates and sticks
20 together at the bottom of a storage vessel over time). The multi-modal emulsions of this invention exhibit a lower tendency to compact than do conventional emulsions.

25 The following examples are given to illustrate the invention and should not be construed as limiting its scope. Unless otherwise indicated, all parts and percentages are by weight.

Example 1 and Comparative Run A

30 An emulsion of a water-soluble polymer and having a bimodal droplet size distribution was prepared as follows.

0130632

Into a 2-liter beaker was added 660.83 g of a 49.2 percent aqueous acrylamide solution, 139.36 g of acrylic acid, 308.31 g of water, and 2.52 g of the pentasodium salt of diethylenetriaminepentaacetic acid (40.2 percent solution). The mixture was stirred on a magnetic stirrer and slowly neutralized using 143.94 g of a 50 percent sodium hydroxide solution.

Using a Waring Blendor® brand mixer, an oil phase was prepared by adding 20.16 g of a 50 percent solution of the isopropanolamide of oleic acid in a liquid hydrocarbon, 10.08 g of sorbitan monooleate, 5.04 g of a polyethylene glycol ether of a secondary alcohol sold by Union Carbide under the trade name Tergitol® 15-S-9, and 459.76 g of a liquid hydrocarbon. This mixture was then stirred for about 10 seconds.

To the oil phase was added 941.3 g of the aqueous phase. An emulsion was prepared by running the Waring Blendor® brand mixer at high speed for 1 minute. This emulsion was added to a jacketed, 2-liter glass reactor and agitated at between 580 and 600 rpm. The remaining 313.7 g of the aqueous phase was added to the emulsion with stirring. The emulsion was purged with nitrogen and agitated for 42 minutes. The agitator speed was reduced to about 60 rpm.

A free radical initiator (0.25 ml of 70 percent t-butyl hydroperoxide and 0.1 percent sulfur dioxide in nitrogen) was added. The emulsion was polymerized as described in U.S. Patent No. 3,284,393 to form a water-in-oil emulsion of an acrylamide/acrylic acid copolymer. The contents of the reactor were drained and filtered and the product had a bimodal size distribution. The product is designated as Example 1.

0130632

A conventional water-in-oil emulsion of an acrylamide/acrylic acid copolymer was prepared as described in U.S. Patent No. 3,284,393 and is designated Comparative Run A. The properties of the emulsion so prepared are compared to those of the bimodal emulsion, Sample No. 1. The results are shown in Table I.

TABLE I

	<u>Sample</u>	<u>Percent Solids¹</u>	<u>Bulk Viscosity²</u>	<u>Percent Clears³</u>	<u>Percent Compacted⁴</u>
10	Ex. 1	35.5	360 (0.360)	0.49	4.7
	Comp. Run A	34.2	560 (0.560)	1.0	9.8

¹Percent Solids is percent of polymer solids in the emulsion.

15 ²In centipoises (pascal second) as measured using a Brookfield RVT, #3 spindle, 10 rpm at 21°C.

20 ³Percent clears is the volume percent of clear layer near the surface of a centrifuge tube after 2 hours centrifugation at 2600 rpm using a Damon IEC Model NH-SII Centrifuge.

25 ⁴Percent compacted is the volume percent of nondispersible polymer which coagulates near the bottom of a centrifuge tube after 2 hours of centrifugation at 2600 rpm as determined by inverting the graduated centrifuge tube and measuring the amount of polymer sticking near the bottom of said tube.

30 The results in Table I indicate that the bimodal emulsion of Example 1 exhibited a lower bulk viscosity, lower percent clears, lower compaction and higher solids content as compared to the emulsion prepared using conventional techniques, Comparative Run A.

0130632

Example 2

An emulsion of a water-soluble polymer and having a bimodal droplet size distribution was prepared as follows.

5 Into a 2-liter beaker was added 703.86 g of a
49.4 percent aqueous acrylamide solution, 149.03 g of
acrylic acid, 332.60 g of water, and 2.68 g of the
pentasodium salt of diethylenetriaminepentaacetic acid
(40.2 percent solution). The mixture was stirred on a
10 magnetic stirrer and slowly neutralized using 153.94 g
of a 50 percent sodium hydroxide solution.

 Using a Waring Blendor® brand mixer, an oil
phase was prepared by adding 17.70 g of a 60.9 percent
solution of the isopropanolamide of oleic acid in a
15 liquid hydrocarbon, 10.78 g of sorbitan monooleate,
5.39 g of a polyethylene glycol ether of a secondary
alcohol sold by Union Carbide under the trade name
Tergitol® 15-S-9, and 384.02 g of a liquid hydrocarbon.
This mixture was then stirred for about 10 seconds.

20 To the oil phase was added 1010.6 g of the
aqueous phase. An emulsion was prepared by running the
Waring Blendor® brand mixer at high speed for 1 minute.
This emulsion was added to a jacketed, 2-liter glass
reactor and agitated at between 400 and 410 rpm. The
25 remaining 331.5 g of the aqueous phase was added to the
emulsion with stirring. The emulsion was purged with
nitrogen and agitated for 42 minutes. The agitator
speed was reduced to about 65 rpm.

30 A free radical initiator (0.25 ml of 70
percent t-butyl hydroperoxide and 0.1 percent sulfur

0130632

dioxide in nitrogen) was added. The emulsion was polymerized as described in U.S. Patent No. 3,284,393 to form a water-in-oil emulsion of an acrylamide/acrylic acid copolymer. The contents of the reactor were
5 drained and filtered and the product had a bimodal size distribution and less than 0.1 percent gel.

Example 3

An emulsion of a water-soluble polymer and having a bimodal droplet size distribution was prepared
10 as follows.

Into a 2-liter beaker was added 241.39 g of a 48.9 percent aqueous acrylamide solution, 37.27 g of a 75 percent aqueous methacryloyloxyethyltrimethyl ammonium chloride, 14.60 g of ammonium chloride, 68.82 g of
15 water and 2.92 g of the penta-sodium salt of diethylene-triaminepentaacetic acid (4 percent solution). The mixture was stirred on a magnetic stirrer and slowly neutralized to a pH of 6.0 with a 50 percent sodium hydroxide solution.

The oil phase was prepared as described in
20 Example 1 by mixing 3.65 g of the isopropanolamide of oleic acid, 3.65 g of sorbitan monooleate, 2.19 g of a polyethylene glycol ether of a secondary alcohol and 125.51 g of a liquid hydrocarbon.

To the oil phase was added 50 percent of the
25 aqueous phase and homogenized using a Waring Blendor® brand mixer at high speed for 30 seconds. The resulting emulsion was placed into a 500-ml resin pot equipped with a motor stirrer and drip pipes. The remaining
30 aqueous portion was added to the emulsion, with stirring,

0130632

at between 300 and 500 rpm. The emulsion was purged with nitrogen and agitated for 45 minutes at 25°C.

To the emulsion was added t-butyl hydroperoxide and 0.1 percent of sulfur dioxide in nitrogen. The exotherm is allowed to reach to between 50° and 55°C in about 1.5 hours. The contents are then heated to 55°C and sparged with 0.1 percent of sulfur dioxide in nitrogen for about 1 hour. The product had a bimodal size distribution.

10 Example 4 and Comparative Run B

A stable emulsion of a water-soluble polymer and having a bimodal droplet size distribution was prepared using techniques described in Example 3 and using materials in amounts as follows.

15 The aqueous phase comprised 309.50 g of a 48.9 percent aqueous acrylamide solution, 47.81 g of a 75 percent aqueous methacryloyloxyethyltrimethyl ammonium chloride, 18.72 g of ammonium chloride, and 3.74 g of the pentasodium salt of diethylenetriamine-
20 pentaacetic acid (4 percent solution).

The oil phase comprised 4.68 g of the isopropanolamide of oleic acid, 4.68 g of sorbitan monooleate, 2.81 g of a polyethylene glycol ether of a secondary alcohol and 110 g of a liquid hydrocarbon.

25 For comparison purposes, an emulsion of a water-soluble polymer was prepared using similar amounts of materials as are described above except that conventional emulsification techniques were employed. The conventionally prepared emulsion gelled and failed.

0130632

That the bimodal emulsion was stable illustrates the superiority of the process of this invention over conventional emulsification techniques which are used in preparing emulsions with reduced oil content
5 and high solids content.

C L A I M S

1. A water-in-oil emulsion ~~polymerization~~ process for preparing polymers of water-soluble monomers which comprises:

- (1) preparing a stable water-in-oil emulsion by:
 - (a) providing an aqueous solution comprising water and at least one water-soluble monomer, .
 - (b) providing an oil solution comprising an inert hydrophobic organic liquid,
 - (c) mixing a portion of the aqueous solution to the oil solution in an amount sufficient to form an aqueous dispersed phase,
 - (d) subjecting the mixture to a shear rate at least sufficient to form a portion of said water-in-oil emulsion,
 - (e) admixing an additional portion of the aqueous solution to the resulting portion of the emulsion previously prepared in an amount sufficient to form an aqueous dispersed phase, and

- (f) subjecting the resulting mixture to a shear rate progressively lower than that employed in forming the previous portion of the emulsion,
- (g) wherein steps (e) and (f) are performed at least once until said water-in-oil emulsion is formed, and
- (2) subjecting the resulting emulsion to polymerization conditions.

2. The process of Claim 1 wherein step (1)(c) comprises mixing a portion of the aqueous solution with a portion of the oil solution in an amount sufficient to form an aqueous dispersed phase, step (1)(e) comprises admixing an additional portion of the aqueous solution to an additional portion of the oil solution in an amount sufficient to form an aqueous dispersed phase, step (1)(f) comprises forming a water-in-oil emulsion by subjecting the resulting mixture to a shear rate progressively lower than that employed in forming the previous portion of the emulsion, and new step (1)(h) comprises mixing portions from steps (1)(d) and (1)(f) together to yield said water-in-oil emulsion.

3. The process of Claim 2 wherein step (1)(h) is omitted, step (2) comprises subjecting each of the water-in-oil emulsions from steps (1)(d) and (1)(f) to polymerization conditions, and new step (3) comprises mixing together the various water-in-oil emulsions of water-soluble polymers.


4. The process of any one of Claims 1, 2 or 3 wherein at least one emulsifying surfactant is incorporated therein.

0130632

5. The process of any one of Claims 1, 2 or 3 wherein at least one emulsifying surfactant and at least one inverting surfactant is incorporated therein.

6. The process of any one of Claims 1, 2 or 3 wherein steps (e) and (f) are performed once.

7. A water-in-oil emulsion of water-soluble polymer prepared by the process of any one of Claims 1, 2 or 3.


 Europäisches Patentamt
 European Patent Office
 Office européen des brevets

(11) Publication number:

0 130 632
A3

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 84200767.6

(51) Int. Cl.⁴: C 08 F 2/32

(22) Date of filing: 25.05.84

(30) Priority: 26.05.83 US 498222

(43) Date of publication of application:
09.01.85 Bulletin 85/2

(88) Date of deferred publication of search report: 02.05.85

(84) Designated Contracting States:
DE FR NL(71) Applicant: THE DOW CHEMICAL COMPANY
Dow Center 2030 Abbott Road Post Office Box 1967
Midland Michigan 48640(US)(72) Inventor: Emerson, Richard R.
628 Hillcrest
Midland Michigan 48640(US)(72) Inventor: Lee, Do Ik
5109 Nakoma Drive
Midland Michigan 48640(US)(72) Inventor: Easterly, James P.
5038 Reinhardt
Bay City Michigan 48706(US)(74) Representative: Urbanus, Henricus Maria, Ir. et al,
c/o Vereenigde Octrooibureaux Nieuwe Parklaan 107
NL-2587 BP 's-Gravenhage(NL)

(54) Water-in-oil emulsion polymerization processes and the water-in-oil emulsions prepared therefrom.

(57) This invention is directed to a water-in-oil emulsion polymerization process for preparing polymers of water-soluble monomers and to the water-in-oil emulsions prepared by the process. The process comprises subjecting portions of the emulsion to varying rates of shear during emulsion formation. Emulsions comprising water-soluble polymers prepared by this process contain a discontinuous aqueous phase having two or more droplet size distributions. These emulsions can have high polymer solids, reduced oil content, low bulk viscosity and high stability.



European Patent
Office

EUROPEAN SEARCH REPORT

0130632

Application number

EP 84 20 0767

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 7)
A,D	US-A-3 996 180 (J. KANE) * Claim 1 *	1	C 08 F 2/32
A	DE-A-2 930 160 (BAYER) * Claim 1 *	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl. 7)
			C 08 F B 01 F
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 19-12-1984	Examiner DEPIJPER R.D.C.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

THIS PAGE BLANK (USPTO)

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☒ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☐ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.

THIS PAGE BLANK (USPTO)